

# Nitrogen superfractionation in dense cloud cores

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## ABSTRACT

We report new calculations of interstellar  $^{15}\text{N}$  fractionation. Previously, we have shown that large enhancements of  $^{15}\text{N}/^{14}\text{N}$  can occur in cold, dense gas where CO is frozen out, but that the existence of an  $\text{NH} + \text{N}$  channel in the dissociative recombination of  $\text{N}_2\text{H}^+$  severely curtails the fractionation. In the light of recent experimental evidence that this channel is in fact negligible, we have reassessed the  $^{15}\text{N}$  chemistry in dense cloud cores. We consider the effects of temperatures below 10 K, and of the presence of large amounts of atomic nitrogen. We also show how the temporal evolution of gas-phase isotope ratios is preserved as spatial heterogeneity in ammonia ice mantles, as monolayers deposited at different times have different isotopic compositions. We demonstrate that the upper layers of this ice may have  $^{15}\text{N}/^{14}\text{N}$  ratios an order of magnitude larger than the underlying elemental value. Converting our ratios to  $\delta$ -values, we obtain  $\delta^{15}\text{N} > 3,000\text{‰}$  in the uppermost layer, with values as high as 10,000‰ in some models. We suggest that this material is the precursor to the  $^{15}\text{N}$  ‘hotspots’ recently discovered in meteorites and IDPs.

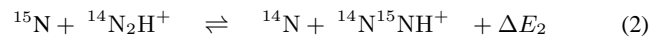
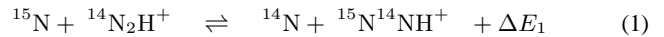
**Key words:** astrochemistry – molecular processes – ISM: molecules – meteors, meteoroids

## 1 INTRODUCTION

Laboratory analyses of primitive solar system materials, such as meteorites, interplanetary dust particles (IDPs), and cometary dust particles returned by the *Stardust* mission, show anomalous fractionation in the heavy isotopes of numerous elements relative to that expected from the cosmic or solar system values (Clayton & Nittler 2004; Lodders & Amari 2005; Alexander et al. 2007; McKeegan et al. 2006). In the case of hydrogen and nitrogen, the large D/H and  $^{15}\text{N}/^{14}\text{N}$  ratios observed in some phases have been attributed to the survival of D- and  $^{15}\text{N}$ -enriched material from the interstellar medium (ISM; Alexander et al. 1998; Messenger 2000). For deuterium, the observed ratios are consistent with models and observations of the ISM, where low-temperature ion-molecule reactions lead to enhanced D/H ratios in both gas- and solid-phase species (e.g. Millar, Bennett & Herbst 1989; Charnley, Tielens & Rodgers 1997.) However, there is little observational data on nitrogen isotope ratios in the ISM, and models of the  $^{15}\text{N}$  fractionation in typical dense clouds predict modest enhancements of  $\sim 25$  per cent (Terzieva & Herbst 2000). In comparison, the largest  $^{15}\text{N}$  enhancements detected in meteorites – in so-called ‘hotspots’ – have  $^{15}\text{N}/^{14}\text{N}$  enhancements of more than a factor of four relative to the Earth (i.e.  $\delta^{15}\text{N} > 3000\text{‰}$ <sup>1</sup>; Busemann et al. 2006). Values of

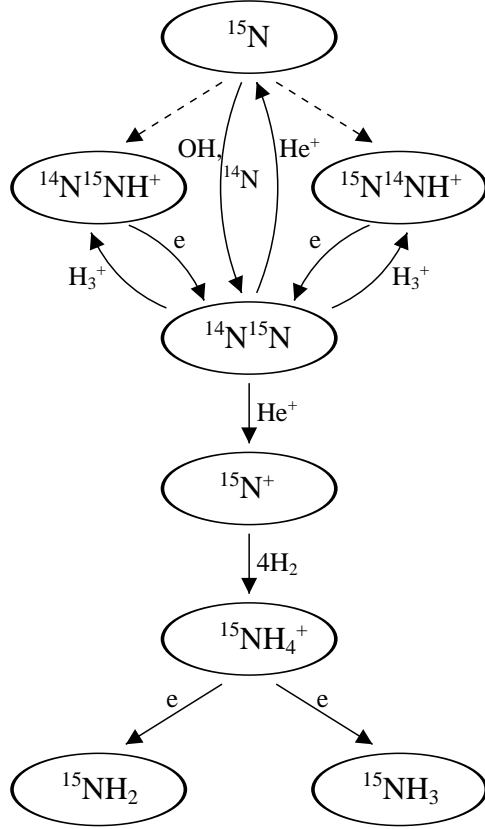
$\delta^{15}\text{N} > 1000\text{‰}$  have also been found in hotspots in IDPs and *Stardust* samples (Floss et al. 2004, 2006; McKeegan et al. 2006).

In an earlier paper we demonstrated that significantly increased  $^{15}\text{N}$  fractionation can occur when CO is depleted onto dust grains (Charnley & Rodgers 2002 [Paper I]). The key fractionation reactions are:



where the exothermicities are  $\Delta E_1 = 27.7\text{ K}$  and  $\Delta E_2 = 36.1\text{ K}$  (Terzieva & Herbst 2000). These preferentially drive  $^{15}\text{N}$  into molecular nitrogen, at the expense of atomic  $\text{N}^0$  which becomes isotopically light. In a standard dark cloud model the degree of fractionation is limited by chemical reactions which cycle nitrogen between atomic and molecular form (see Fig. 1). However, if CO is frozen out as ice, OH is unavailable, this cycle is broken, and much larger  $^{15}\text{N}$ -enhancements are possible. In this scenario, degradation of the ( $^{15}\text{N}$ -enriched)  $\text{N}_2$  by  $\text{He}^+$  is essentially a one-way process. The  $\text{N}^0$  atoms released by this reaction remain in the gas, whereas the  $\text{N}^+$  ions react rapidly with  $\text{H}_2$  in a sequence of reactions to form ammonium (Fig. 1). The  $\text{NH}_4^+$  ions then recombine with electrons, producing  $\text{NH}_2$  and  $\text{NH}_3$ , which subsequently freeze out on the dust grains. If the solid-phase  $\text{NH}_2$  radicals are hydrogenated to  $\text{NH}_3$ , as expected from models of grain surface chemistry (Brown & Charnley 1990), the end result is a large abundance of isotopically heavy ammonia ice. At late times in this model, when  $\text{N}^0/\text{N}_2 > 1$ , the efficiency of reactions (1) and (2) are greatly increased, leading to much larger gas-phase  $^{15}\text{N}/^{14}\text{N}$

<sup>1</sup>  $\delta^{15}\text{N}(\text{X}) \equiv 1000 \times \left[ \left( ^{15}\text{N}/^{14}\text{N} \right)_{\text{X}} / \left( ^{15}\text{N}/^{14}\text{N} \right)_{\oplus} - 1 \right]$  where  $\left( ^{15}\text{N}/^{14}\text{N} \right)_{\oplus}$  is the terrestrial isotopic ratio of 0.003678 (De Bièvre et al. 1996)



**Figure 1.** Principal gas-phase reactions involving nitrogen. The dotted lines indicate the fractionation reactions (1) and (2).

ratios than in the standard dense cloud chemistry. Ultimately, we found that the ammonia ice is enhanced in  $^{15}\text{N}$  by a factor of 1.8.

This model could account for the presence of high bulk  $\delta^{15}\text{N}$  values in IDPs (Messenger 2000), and was also able to account for the non-detection of  $\text{N}_2$  in comets. Some additional processing was indicated to incorporate the  $^{15}\text{N}$ -enriched ammonia into the carbonaceous matter, and secondary energetic processing to add  $^{15}\text{NH}_2$  side-groups to polycyclic aromatic hydrocarbon (PAH) molecules was suggested. Recent meteoritic studies have confirmed that most of the  $^{15}\text{N}$  enrichment in IDPs is carried by amine side-groups on aromatic moieties (Keller et al. 2004). However, the model was unable to reproduce the largest  $\delta^{15}\text{N}$  values seen in the hotspots. Moreover, the experimental determination by Geppert et al. (2004) that recombination of  $\text{N}_2\text{H}^+$  preferentially breaks the  $\text{N}\equiv\text{N}$  bond, producing  $\text{N}^0$  and  $\text{NH}$ , acts to suppress the maximum fractionation (Rodgers & Charnley 2004 [Paper II]).

In this paper, we are motivated to revisit our previous models as a result of several recent discoveries. Firstly, the experimental results of Geppert et al. (2004) have been challenged by Molek et al. (2007), who demonstrated that recombination of  $\text{N}_2\text{H}^+$  leads predominantly to  $\text{N}_2 + \text{H}$ , as indicated in previous work (Adams et al. 1991). The new results indicate that rupture of the  $\text{N}_2$  bond occurs rarely, if at all, with an upper limit for the  $\text{NH} + \text{N}^0$  branching ratio of 5 per cent. Secondly, observations of several pre-stellar cores have revealed that they have temperatures below 10 K in their central, densest regions, as expected from physical models (Evans et al. 2001; Zucconi, Walmsley & Galli 2001). For example, Crapsi

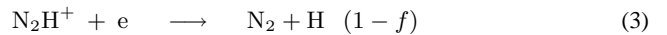
et al. (2007) derived  $T = 5.5$  K in L1544, and Pagani et al. (2007) found  $T = 7$  K in L134N. Due to the small zero-point energy changes associated with  $^{15}\text{N}$  fractionation, reactions (1) and (2) are extremely sensitive to temperature, and these lower temperatures may be expected to yield larger  $^{15}\text{N}/^{14}\text{N}$  ratios.

Thirdly, observations of  $\text{N}_2\text{H}^+$  in dark clouds imply  $\text{N}_2$  abundances of a few  $\times 10^{-6}$  (Womack, Ziurys & Wyckoff 1992; Maret, Bergin & Lada 2006). This is significantly less than the galactic elemental nitrogen abundance and Maret et al. proposed that the ‘missing’ nitrogen was in atomic form. Although the chemical model of Maret et al. assumed the Geppert et al. (2004) branching ratios for  $\text{N}_2\text{H}^+$  recombination, models assuming the ‘old’ branching ratio also predict  $\text{N}^0 > \text{N}_2$  at early times (e.g. Pineau des Forêts, Roueff & Flower 1990). This is because  $\text{N} \rightarrow \text{N}_2$  conversion occurs via neutral-neutral reactions, and the time-scale for this process,  $t_{\text{N}_2}$ , is larger than the dynamical free-fall time,  $t_{\text{ff}}$ . In contrast, CO is formed fairly rapidly by ion-molecule chemistry, on a time-scale  $t_{\text{CO}}$ , where  $t_{\text{CO}} < t_{\text{ff}} < t_{\text{N}_2}$ . Therefore, we would expect young clouds to have high CO abundances but relatively small  $\text{N}_2/\text{N}$  ratios. This is consistent with the view that molecular clouds and pre-stellar cores form rapidly, on a time-scale of order a few times the free-fall time (Ballesteros-Paredes et al. 2007). Dynamical-chemical models of collapsing clouds show that  $\text{N} \rightarrow \text{N}_2$  conversion is never efficient over  $t_{\text{ff}}$  (Brown, Charnley & Millar 1988). As discussed above, a large  $\text{N}^0/\text{N}_2$  ratio is necessary to produce substantial  $^{15}\text{N}$ -fractionation, so if the nitrogen in dense clouds is in fact mainly atomic rather than molecular, this will have important consequences for the  $^{15}\text{N}/^{14}\text{N}$  ratios.

Finally, in our earlier work we only calculated the bulk isotope ratios in the ammonia ice. In reality, the grain mantles will have an ‘onion-ring’-like structure consisting of sequentially accreted monolayers. Thus, temporal variations in the gas-phase  $^{15}\text{N}/^{14}\text{N}$  ratios will be preserved as spatial gradients in the ices, with each layer recording the gas-phase ratio at the time it was accreted. In particular, the late-accreting, uppermost layers will be the most highly fractionated. As it is these layers which are likely to experience the largest degree of subsequent processing, it is necessary to distinguish between the bulk isotope ratios in the ice as a whole, and those in specific monolayers.

## 2 MODEL

We utilize the same chemical model as in our previous work (Papers I & II). The  $^{15}\text{N}$ -fractionation chemistry is based on Terzieva & Herbst (2000); a list of the reactions and the rate coefficients we have adopted appeared in Paper II. We consider a high density core ( $n_{\text{H}_2} = 5 \times 10^6 \text{ cm}^{-3}$ ) with temperatures of 5, 7, and 10 K, and a cosmic ray ionization rate of  $5 \times 10^{-17} \text{ s}^{-1}$ . The elemental  $^{15}\text{N}/^{14}\text{N}$  ratio in each model is generally assumed to be 1/400, although the effects of using other values were also investigated. A key parameter is the branching ratio for the dissociative recombination of  $\text{N}_2\text{H}^+$ :



We considered values for  $f = 0.0, 0.02$ , and  $0.05$ , based on the experimental results of Molek et al. (2007). We use elemental abundances for C, O, and N of 140, 290, and 80 parts per million respectively, relative to hydrogen (Savage & Sembach 1996), and assume complete depletion of metals. All the carbon is initially in the form of CO, and the remaining oxygen is atomic.

As before, we assume that CO freezes out onto grains with a sticking coefficient of unity, whereas N and N<sub>2</sub> remain in the gas. The reason for this selective depletion of CO versus N<sub>2</sub> is controversial, as laboratory experiments reveal that the two species have similar binding energies (Öberg et al. 2005). Nevertheless, observations of pre-stellar cores show ample evidence for the presence of N<sub>2</sub>-rich, CO-poor regions toward the centers of these objects (Bergin & Tafalla 2007). Due to their low polarizabilities, atoms should have the lowest binding energies for physisorption to icy dust grains. Reaction with an H atom forms a simple hydride that can stick more effectively due to hydrogen bonding with the substrate. Thus, we assume that O atoms are hydrogenated on the grains to form water ice. Conversely, recent laboratory experiments indicate a very low efficiency for the reaction of N<sup>0</sup> and H on ice surfaces (T Hiraoka, private communication), which supports our assumption that N atoms do not stick.

We have adapted our model to track the <sup>15</sup>N/<sup>14</sup>N ratios as successive monolayers (ML) of ammonia ice are accreted. A ‘typical’ interstellar grain of size 0.1 μm has ~ 10<sup>6</sup> surface sites, and an abundance relative to hydrogen of ~ 10<sup>-12</sup>. Hence, one ML corresponds to a total solid phase abundance of 10<sup>-6</sup>, and our elemental N abundance corresponds to a maximum of 80 ML of ice, assuming that all the nitrogen freezes out as NH<sub>3</sub> (or NH<sub>2</sub>). In fact, a large fraction of the nitrogen remains in the gas phase in the form of N<sup>0</sup>, and we typically find that we form ~ 30 ML of ammonia ice.

### 3 RESULTS

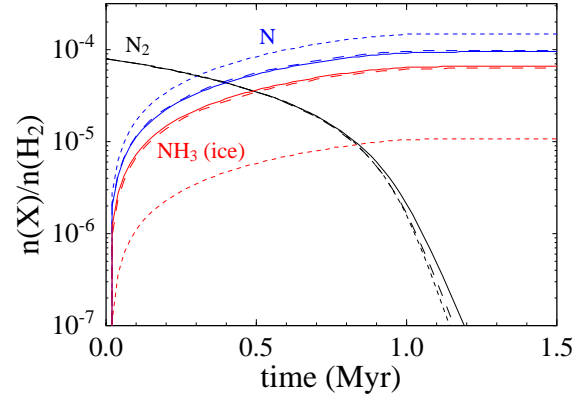
We began by investigating the importance of the branching ratio,  $f$ , in the recombination of N<sub>2</sub>H<sup>+</sup>. We found only very small differences in the results of models with  $f$  equal to 5, 2, and 0 per cent, and conclude that, as long as  $f \leq 0.05$ , the presence of channel (4) does not significantly affect the <sup>15</sup>N chemistry. We then varied the elemental nitrogen isotope ratio, using values for <sup>14</sup>N/<sup>15</sup>N of 800, 400, and 100. In every case, the <sup>15</sup>N enhancements are identical, relative to the underlying ratio. Henceforth, we discuss models with  $f = 0.02$  and <sup>14</sup>N/<sup>15</sup>N = 400.

#### 3.1 Temperature dependence

Figure 2 shows the abundances of the three main repositories of nitrogen – gaseous N<sup>0</sup> and N<sub>2</sub>, and solid NH<sub>3</sub> – as a function of time, assuming that all of the nitrogen is initially present as N<sub>2</sub>. The overall nitrogen chemistry is the same at 10 K and 7 K: N<sub>2</sub> is degraded on a time-scale ~ Myr. At late times just over half of the total nitrogen is in the gas phase as atoms, and just under half has frozen out as ammonia ice. At 5 K, however, very little ice is formed, due to the endo-ergicity of the reaction

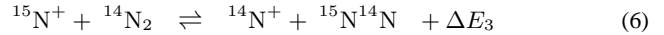


We have assumed an activation energy barrier of 85 K for this reaction, based on the value in the UMIST reaction rate database (Woodall et al. 2007). At 5 K, the reaction becomes so slow that radiative recombination becomes the dominant loss route for N<sup>+</sup> ions, and only small amounts of gas-phase NH<sub>2</sub> and NH<sub>3</sub> are produced. In effect, the barrier for reaction (5) sets a limit on the nitrogen chemistry in that, as the temperature drops, it eventually becomes too cold to produce ammonia. In extremely cold cores the chemistry simply transforms the initial gas-phase N<sub>2</sub> into gas-phase N<sup>0</sup>. In the following, we therefore look at the fractionation in 7 K and 10 K gas.



**Figure 2.** Time evolution of the main nitrogen carriers when all the N is initially molecular. Solid, dashed and dotted lines correspond to  $T = 10$ , 7, and 5 K respectively.

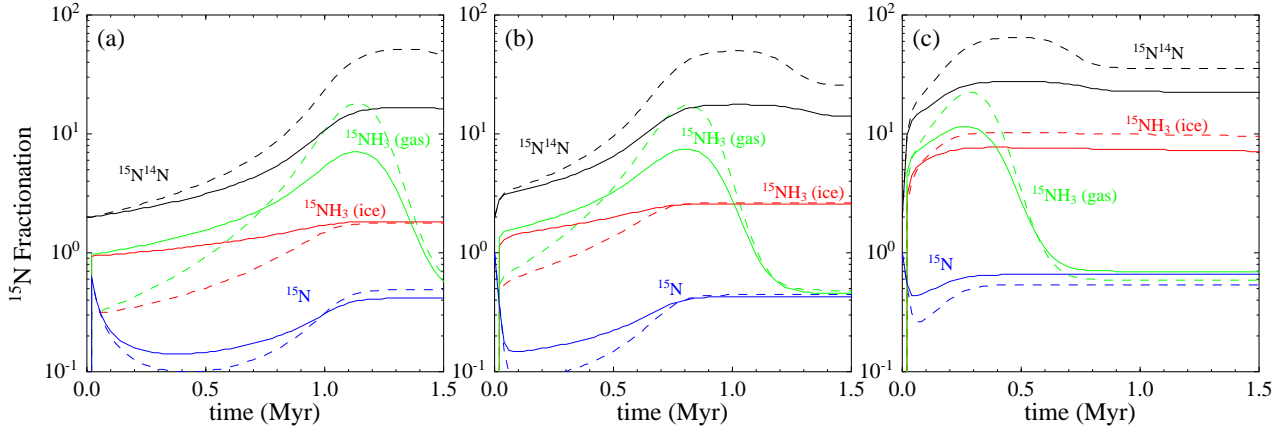
Figure 3a shows the fractionation in the most important molecules. The results for 10 K gas are similar to those shown in Paper I, whereas at 7 K significantly larger peak <sup>15</sup>N/<sup>14</sup>N ratios are found in gas-phase NH<sub>3</sub> and N<sub>2</sub>. At early times, the gas-phase ammonia formed at 7 K is actually *depleted* in <sup>15</sup>N. This is due to the reduced rate of reaction (5) which leads to a much larger N<sup>+</sup> abundance than at 10 K. These N<sup>+</sup> ions undergo isotope-exchange reactions with N<sub>2</sub> (Freysinger et al. 1994):



where  $\Delta E_3 = 28.3$  K (Terzieva & Herbst 2000). This reaction shuffles <sup>15</sup>N back into N<sub>2</sub>, reducing the <sup>15</sup>N-fractionation in N<sup>+</sup> and thus ammonia. At late times, this effect is still suppressing the N<sup>+</sup> fractionation relative to N<sub>2</sub>, but the enormous <sup>15</sup>N-enhancements in N<sub>2</sub> ensures that N<sup>+</sup> and NH<sub>3</sub> are more fractionated than at 10 K. In terms of the bulk <sup>15</sup>N/<sup>14</sup>N ratio in the ammonia ice, both the 10 K and 7 K models predict similar enhancements of ~ 1.8. However, as discussed earlier, the time evolution of the isotope ratios will be preserved in the layered structure of the ices. Even though the overall icy <sup>15</sup>N/<sup>14</sup>N ratios are the same in both models, ammonia ices which accreted at 7 K will have a more heterogeneous structure, with the innermost layers depleted in <sup>15</sup>N, but with the top layers enhanced by factors ~ 10.

#### 3.2 The initial N/N<sub>2</sub> ratio

Significant fractionation in N<sub>2</sub> can only occur when N<sub>2</sub> is not the dominant nitrogen carrier. In the models discussed so far, this occurs at late times when most of the N<sub>2</sub> has been broken down by He<sup>+</sup> attack, on time-scales ~ Myr. However, if a substantial fraction of the nitrogen is initially atomic, enhanced <sup>15</sup>N/<sup>14</sup>N ratios can be produced on much shorter time-scales. The N<sup>0</sup>/N<sub>2</sub> ratio at  $t = 0$  depends on the dynamical and chemical history of the cloud before the formation of the dense pre-stellar core, and can be taken as a free parameter in our model. To investigate the importance of this factor, we have considered three additional models, where the initial fraction of N in molecular form is taken to be 0.6, 0.1, and 0. The latter case, where all of the nitrogen is initially atomic, is not particularly realistic, but was used to constrain the amount of N<sub>2</sub> that can be synthesized from N<sup>0</sup> in the limited time available be-



**Figure 3.** Time evolution of the  $^{15}\text{N}/^{14}\text{N}$  enhancement ratios in key species at  $T = 10$  K (solid lines) and  $T = 7$  K (dashed lines). The initial fraction of nitrogen in molecular form is 100%, 63%, and 10% in panels (a), (b), and (c) respectively.

fore CO etc. freeze out. We find that this produces only very small  $\text{N}_2$  abundances,  $\approx 2$  per cent of the total nitrogen. This means that the available pool of  $\text{N}_2$  – roughly half of which will end up as ammonia ice – is essentially equal to the  $\text{N}_2$  abundance at  $t = 0$ .

Figure 3b and 3c shows the isotope chemistry when a large fraction of the original nitrogen is atomic. Qualitatively, the gas-phase  $\text{N}_2$  and  $\text{NH}_3$  fractionation is similar to that in fig. 3a, except that the peak  $^{15}\text{N}/^{14}\text{N}$  ratios occur much earlier as the initial  $\text{N}_2$  abundance is reduced. As before, we find that the upper layers of the ice should be enhanced in  $^{15}\text{N}$  by an order of magnitude. In terms of the overall bulk isotope ratio in the ice, it is clear that much larger values result, with  $(^{15}\text{NH}_3/^{14}\text{NH}_3)_{\text{ice}} = 7$  when only ten per cent of the initial nitrogen is molecular. This is due to the fact that less ammonia ice is formed overall, so the highly-fractionated upper layers account for a greater proportion of the total ice. We find roughly the same peak ratios regardless of the initial  $\text{N}^0/\text{N}_2$  ratio, but in models with more  $\text{N}_2$  the bulk fractionation is diluted by the large number of monolayers which accrete at early times with essentially normal (or even reduced in the 7 K model)  $^{15}\text{N}/^{14}\text{N}$  ratios.

### 3.3 Isotope ratios in individual monolayers

We have calculated the  $^{15}\text{N}/^{14}\text{N}$  in successive ML as they accrete from the gas. For comparison with laboratory measurements, we have converted the isotopic ratios into  $\delta$ -values relative to the terrestrial  $^{15}\text{N}/^{14}\text{N}$  ratio. In order to do this, we need to know the original  $^{15}\text{N}/^{14}\text{N}$  ratio in the material from which the protosolar nebula (PSN) was formed. We assume a value of  $(^{15}\text{N}/^{14}\text{N})_{\text{PSN}} = 0.0025$ , which is implied by three independent measurements: Jupiter’s atmosphere, high-temperature nebular condensates, and the solar wind (Fouchet et al. 2004; Meibom et al. 2007; Kallenbach, Bamert & Hilchenbach 2007.) Figure 4 shows the  $\delta$ -values in different ML for several models. Clearly, the upper layers of the ice are the most highly fractionated, with peak values of  $\delta^{15}\text{N} > 3000$  ‰ in every case. Also apparent is the approximate proportionality between the initial  $\text{N}_2$  abundance and the total number of ML that accrete. When only ten per cent of the nitrogen is initially molecular, only four ML of  $\text{NH}_3$  ice are formed. However, in this case every ML is very highly fractionated, with  $\delta^{15}\text{N}$  everywhere greater than 2000 ‰. As discussed in §3.1, the peak values

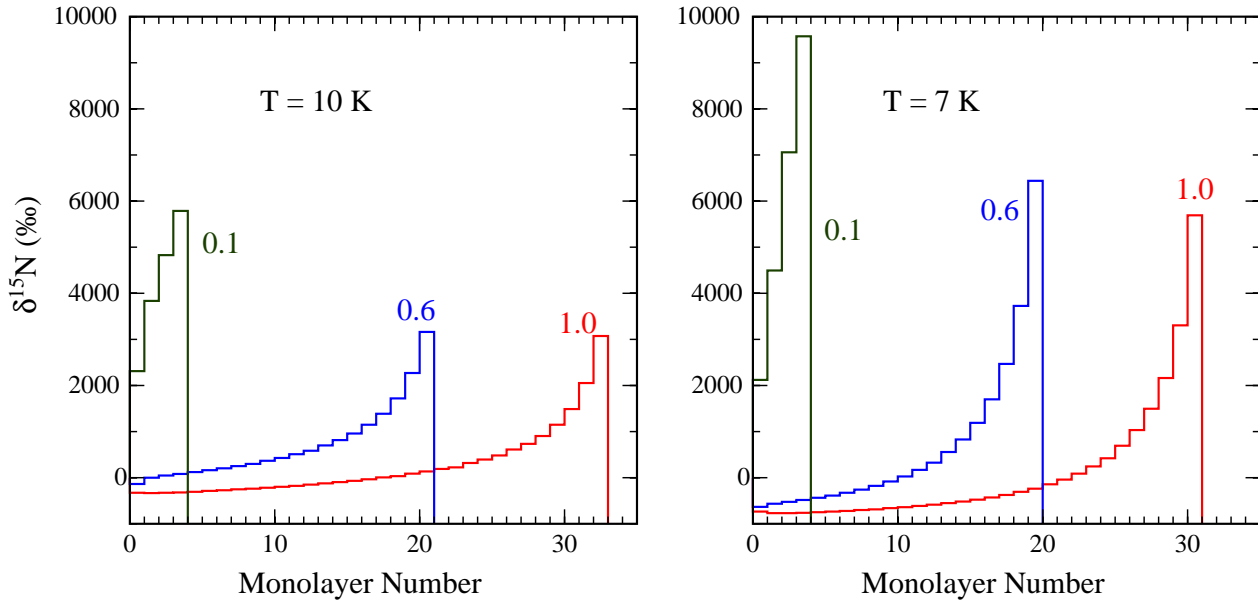
are larger for  $T = 7$  K, but the 7 K model also produces a large number of ML at early times that are slightly depleted in  $^{15}\text{N}$ .

## 4 CONCLUSIONS

We have revisited our earlier work on  $^{15}\text{N}$  fractionation based on recent experimental and observation results. Using the branching ratios for  $\text{N}_2\text{H}^+$  dissociative recombination derived by Molek et al. (2007), we effectively recover the results of our earlier work in dense, CO-depleted gas at 10 K (Paper I.) We have investigated the effects of varying the temperature, and show that at lower temperatures, larger  $^{15}\text{N}/^{14}\text{N}$  ratios are produced in gas-phase in  $\text{N}_2$ . However, the barrier for the reaction of  $\text{N}^+$  ions with  $\text{H}_2$  sets a lower limit on the temperature at which ammonia can be produced efficiently. Assuming the ‘standard’ rate coefficient for this reaction we find that very little ammonia ice is generated for  $T < 7$  K. We have also looked at the effects of a substantial  $\text{N}^0/\text{N}_2$  ratio at  $t = 0$ . We find that, because roughly half of the initial  $\text{N}_2$  ends up in the form of  $\text{NH}_3$  and  $\text{NH}_2$ , reduced molecular nitrogen abundances yield less ammonia ice in total. Smaller  $\text{N}^0/\text{N}_2$  ratios do not significantly affect the peak gas-phase fractionation ratios, but because the highly-fractionated ammonia formed at late times represents a greater proportion of the total ice, we find that the bulk ice  $^{15}\text{N}/^{14}\text{N}$  ratio can be greatly increased.

Following the  $^{15}\text{N}/^{14}\text{N}$  ratios in individual monolayers as they accrete sequentially from the gas, we have shown that gas-phase temporal variations in isotopic ratios are preserved as spatial gradients in the layered ammonia ice. The uppermost layers which accrete at late times have the largest  $^{15}\text{N}$ -enhancements, up to an order of magnitude with respect to the elemental  $^{15}\text{N}/^{14}\text{N}$  ratio. Converting to  $\delta$ -values to compare with laboratory determinations of the isotope ratios in primitive solar system materials, we derive peak values of  $\delta^{15}\text{N} > 3000$  ‰ in gas at 10 K, and values as large as  $\delta^{15}\text{N} \sim 10000$  ‰ in models with lower temperatures and smaller  $\text{N}^0/\text{N}_2$  ratios. This is more than sufficient to account for the largest measured ratios, and demonstrates that interstellar gas-phase chemistry is likely the ultimate source of cometary and meteoritic  $^{15}\text{N}$  anomalies.

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**Figure 4.**  $\delta^{15}\text{N}$  values in different monolayers, for  $T = 10\text{ K}$  and  $T = 7\text{ K}$ . Labels refer to the fraction of nitrogen initially assumed to be molecular.

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## REFERENCES

- Adams N. G. et al., 1991, *J Chem. Phys.*, 94, 4852
- Alexander C. M. O'D., Russell S. S., Arden J. W., Ash R. D., Grady M. M., Pillinger C. T., 1998, *Meteoritics & Planet. Sci.*, 33, 603
- Alexander C. M. O'D., Boss A. P., Keller L. P., Nuth J. A., Weinberger A., 2007, in Reipurth B. et al., eds., *Protostars and Planets V*, U. Arizona Press, Tucson, p. 801
- Ballesteros-Paredes J., Klessen R. S., Mac Low M.-M., Vazquez-Semadeni E., 2007, in Reipurth B. et al., eds., *Protostars and Planets V*, U. Arizona Press, Tucson, p. 63
- Bergin E. A., Tafalla M., 2007, *ARA&A*, 45, 339
- Brown P.D., Charnley S.B., Millar T.J., 1988, *MNRAS*, 231, 409
- Brown P.D., Charnley S.B., 1990, *MNRAS*, 244, 432
- Busemann H., Young A. F., Alexander C. M. O'D., Hoppe P., Mukhopadhyay S., Nittler L. R., 2006, *Sci.*, 312, 727
- Charnley S.B., Rodgers S.D., 2002, *ApJ*, 569, L133 (Paper I)
- Charnley S.B., Tielens A.G.G.M., Rodgers S.D., 1997, 482, L203
- Clayton D. D., Nittler L. R., 2004, *ARA&A*, 42, 39
- Crapsi A., Caselli P., Walmsley M. C., Tafalla M., 2007, *A&A*, 470, 221
- De Bièvre P., Valkiers S., Peiser H. S., Taylor P. D. P., Hansen P., 1996, *Metrologia*, 33, 447
- Evans N. J. II, Rawlings J. M. C., Shirley Y. L., Mundy L. G., 2001, *ApJ*, 557, 193
- Floss C., Stadermann F. J., Bradley J. P., Dai Z. R., Bajt S., Graham G., 2004, *Sci.*, 303, 1355
- Floss C., Stadermann F. J., Bradley J. P., Dai Z. R., Bajt S., Graham G., Lea A. S., 2006, *Geo. Cosmo. Acta*, 70, 2371
- Fouchet T., Irwin P. G. J., Parrish P., Calcutt S. B., Taylor F. W., Nixon C. A., Owen T., 2004, *Icarus*, 172, 50
- Freysinger W., Khan F.A., Armentrout P.B., Tosi P., Dmitriev O., Bassi D., 1994, *J. Chem. Phys.*, 101, 3688
- Geppert W. D. et al., 2004, *ApJ*, 609, 459
- Kallenbach R., Bamert K., Hilchenbach M., 2007, *Space Sci. Rev.*, in press
- Keller L. P., Messenger S., Flynn G. J., Clemett S., Wirick S., Jacobsen, C., 2004, *Geo. Cosmo. Acta*, 68, 2577
- Lodders K., Amari S., 2005, *Chemie der Erde*, 65, 93
- Maret S., Bergin E.A., Lada C., 2006, *Nature*, 442, 425
- McKeegan K. D. et al., 2006, *Sci.*, 314, 1724
- Meibom A., Krot A. N., Robert F., Mostefaoui S., Russell S. S., Petaev M. I., Gounelle M., 2007, *ApJ*, 656, L33
- Messenger S., 2000, *Nature*, 404, 968
- Millar T. J., Bennett A., Herbst E., 1989, *ApJ*, 340, 906
- Molek C.D., McLain J.L., Poteyra V., Adams N.G., 2007, *J. Phys. Chem. A*, 111, 6760
- Öberg K. I., van Broekhuizen F., Fraser H. J., Bisschop S. E., van Dishoeck E. F., Schlemmer S., 2005, *ApJ*, 621, L33
- Pagani L., Bacmann A., Cabrit S., Vastel C., 2007, *A&A*, 467, 179
- Pineau des Forêts G., Roueff E., Flower D. R., 1990, *MNRAS*, 244, 668
- Rodgers S. D., Charnley S. B., 2004, *MNRAS*, 352, 600 (Paper II)
- Savage B. D., Sembach K. R., 1996, *ARA&A*, 34, 279
- Terzieva R., Herbst E., 2000, *MNRAS*, 317, 563
- Womack M., Ziurys L. M., Wyckoff S., 1992, *ApJ*, 393, 188
- Woodall J., Agúndez M., Markwick-Kemper A. J., Millar T. J., 2007, *A&A*, 466, 1197
- Zucconi A., Walmsley C. M., Galli D., 2001, *A&A*, 376, 650